CO_2 CAPTURE FOR MINERALIZED MISCANTHUS AGGREGATES

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ABSTRACT

At a time when the cement industry is largely responsible for the production of CO_2 in the construction sector, it is useful to make this production a reverse phenomenon: that's CO_2 capture. The CO_2 absorption process called carbonation, improves specific properties of the concrete during the conversion of carbon dioxide CO_2 into calcium carbonate $CaCO_3$. Current environmental concerns motivate the study of carbonation in order to maximize the absorption of carbon dioxide.

Experimentation has been performed on bio-based and recycled concrete aggregates. The long term stability as well as the reinforcement of bio-based aggregates – miscanthus - may be obtained by means of a mineralization process of the natural product: a preparation with a lime and/or cement-based material is necessary to reinforce the cohesion of the bio-based product. Specific conditions for CO_2 capture have been tested and concrete blocks have been produced with aggregates. Performances of aggregates and concrete blocks before and after carbonation are presented and show increasing performances in specific situations of CO_2 capture.

1. INTRODUCTION

The carbonation process has been already studied in order to improve the dimensional stability of concrete building blocks. Indeed, the hardened cement paste reacts with atmospheric CO_2, which can lead to problems of withdrawal. In the U.S., the NCMA (National Concrete Masonry Association) and the PCA (Portland Cement Association) have conducted research in 1963: the concrete blocks were first subjected to moist air between 80 and 100 °C for 5 to 18 hours. Then, after 24 hours or four months, they were stored a high atmospheric CO_2 [1]. This helped to reduce shrinkage of about 30%. But the energy consumption of this process is enormous.

During Seventies, mechanisms of carbonation were studied in relation with reactivity and strength of calcium silicate activated by CO_2 [2]. This technique was introduced for the production of panels cement fibre based, in order to reduce the manufacturing time; the first plant operating on this principle was built in Hungary in 1985, but was closed for reasons of cost of CO_2.

A feasibility study of CO_2 sequestration through a technique of accelerated cure was conducted at McGill University (Montreal, Canada) between 2004 and 2006 [3]. The possibilities of fixing CO_2 in cement matrices were explored and performances in the short

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and long term implications were verified: it showed some interesting opportunities offered by this technique, based on specific accelerated carbonation process.

Currently, concrete blocks are produced on a wet cure (water vapor) based process. It is estimated that for 1 m³ of concrete blocks manufacturing, wet cure at atmospheric pressure consumes 0.59 GJ while curing in autoclave consumes 0.71GJ [3, 4]. If a CO_2 injection process is put in place, for the same volume of concrete, the energy for recovery and compression of CO_2 is estimated to be 0.02-0.10GJ / m³, for a minimum value of CO_2 capture into cement of 10 and 50%, respectively. That means that the total energy, excluding CO_2 transport necessary to carbonation, is significantly lower than that required for a traditional wet cure.

The building blocks of concrete are particularly suited to carbonation, because of their mass production, their high porosity and the need to practice a wet cure. The reaction between the cement paste at early age and carbon dioxide thus constitutes a form of CO_2 sequestration. If we consider a hollow block 39x19x19cm and 18kg, which contains about 10% by mass of cement, we can consider that it is able to fix at least 0.18kg of CO_2 [3]. If the cement is replaced by slag, the capture rate will remain about the same [4]. Furthermore, if the aggregate (86% by mass) are also used to fix CO_2, the fixed amount considerably increases. Carbonated steel slag could set another 6% by mass. Therefore, if one considers that each aggregate is able to fix about 5% of its mass in CO_2, a total sequestration of 0.77kg may be attempted, for aggregates and a block. A block of concrete construction would be potentially able to fix 0.95kg of CO_2; as production of concrete blocks in Belgium is 3.36 million tonnes per year (*www.febe.be*), it is estimated that the amount of CO_2 fixed could be 16,800 tons, if only 5% of the Belgian market is concerned in a first step. On the other hand, considering that 1 m² wall consumes 12.5 (39x19x19cm) blocks, we can estimate that each m² of wall will be able to capture 2.25 kg CO_2. For comparison, in Canada and the USA, the annual sequestration potential is estimated at 3.2 million tons [3].

This concept could lead to term, if based on the judicious choice of materials for the "aggregate" part, to a situation of "zero-emission". This will be the case if bio-sourced or recycled aggregates can be used [5, 6, 7]. Moreover, the accelerated carbonation blocks should lead to improved mechanical performances, lower porosity and a reduced risk of efflorescence: the denser microstructure of concrete, which improves the durability of the product and, therefore, the duration of life. Finally, the developed industrial process does not change the potential for recycling at end of life, particularly in the manufacture of new blocks.

The objectives of the present research are to study the opportunity of the capture of CO_2 in concrete blocks with miscanthus mineralized aggregates. Mineralization process is described as well as the way of producing blocks for CO_2 capture by means of accelerated carbonation.

2. MATERIALS

Compared to the hemp plant (annual) [8, 9], miscanthus is a perennial plant, located for several years (up to 20 years), which reduces costs of crop establishment: energy consumption is evaluated around 9223 GJ/ha (for hemp: 13 298 GJ/ha).

In comparison with wood, miscanthus has a high content of parenchyma, surrounded by a though fibrous structure. It therefore combines a high rigidity with a low density [10]. The modulus of elasticity of Miscanthus Giganteus varies between 2 and 8 GPa [11].

The strength and the physical properties of agro-materials are coming from their *ultra-structure*. The different layers that constitute the cell wall of plant [12] show the complex interactions between the cellulose material and binder necessary to combine these particles and homogenize the behavior of the finished material. In our case, the inorganic binder, based on hydraulic or pozzolanic products, offers a variable behavior depending on water content but also on sugar or carbohydrates concentration. Wooden structure is a highly porous and very durable material but it seems essential to be treated before used as aggregate in concrete [12]. Indeed, without woodchip pretreatments, the mixtures offer unstable results [13]. In addition, the stability of the concrete cannot be achieved because untreated chips react chemically with the environment and dimensions considerably vary with changes in humidity. In order to increase the durability of the composite and to reduce vapor or liquid transfers between the chips and their environment, the mineralization appears to be the best solution [14].

This treatment consists in soaking the chips with a mineral solution; a mixing procedure of about 3 min allows an impregnation of the chips. Currently, the components used for mineralization are mainly calcium chloride, silica fume and derivatives of lime and cement. The type of mineralization is obviously an important factor to be considered: the products on the market are cement, but also lime and by-products of the steel industry, electricity production (ash) or extractive industries (limestone filler). For applications in building interior, the use of gypsum waste may be also considered. The studies we conducted until now [12, 13] promote the use of mixtures of cement and lime. Mineralization induces a reduction of absorption rate and a higher E modulus, which is convenient for using as aggregate [14].

The selected pretreatment is based on the mineralization of the miscanthus aggregate which is coated with cement and silica fume [12], in the following proportions (Table 1).

Table 1 Mix proportions for mineralization

Components	Quantity (g)	Quantity (wt %)
Miscanthus aggregates	1000	31.12
Cement CEM I 52.5 N	900	28.01
Water	1050	32.68
Superplasticizer	3	0.09
Silica Fume	250	7.78
$CaCl_2$	10	0.31

Components are mixed in the following manner:

- introduce 80 liters of miscanthus aggregates and the silica fume into the mixer and mix for 30 seconds;
- add half of the water, in which $CaCl_2$ has been first dissolved, and mix for 30 seconds;
- add cement and the rest of the water, in which superplasticizer has been dissolved;
- after 2 minutes of mixing, spread the aggregates to a thickness of 5 cm for drying.

Once aggregates are mineralized, a part of them is placed in the ambient environment (20°C, 60% RH), the other part in the incubator, during 48h.

3. CONCRETE BLOCKS PREPARATION

Concrete blocks can then be produced with CEM I 52.5 N according to the proportions given in Table 2.

Table 2 Mix proportions for miscanthus concrete blocks

Components	Quantity (%)	Quantity (g/block)
Mineralized miscanthus aggregates	49.18	1335
Cement CEM I 52.5 N	29.51	803
Water	21.31	577

Mixing procedure for concrete blocks is described hereafter and is inspired by the work realized by William Rosolen [13]:

- introduce mineralized miscanthus aggregates and dampening water into the mixer and mix for 60 seconds;
- add cement and mix for 60 seconds;
- add mixing water and mix for 60 seconds.

The steps of vibration are as follows (Fig. 1a):

- place the mold on the vibrating table (50 Hz);
- cast half of the fresh concrete in the cubic metal mold;
- put a mass (± 8 kg) in the mold on the fresh concrete;
- set the vibrating table on for a period of 30 seconds;
- remove the mass;
- cast the other half of the fresh concrete in mold;
- place the mass of 8 kg in the mold of the fresh concrete;
- set the vibrating table on for 30 seconds;
- remove the samples (Fig. 1b);

a) (b)

Figure 1: Preparation of the samples (a) vibration and loading principles, (b) demoulding of the concrete blocks

4. CO_2 INJECTION TECHNIQUE

The objective of the CO_2 injection technique procedure is the development of a system able to force carbonation. An air-conditioned room called *incubator*, with controlled humidity and temperature, will be used. Specific CO_2 injection system is connected to the incubator (Fig. 2). The following three parameters can be taken into account by the latter: the temperature, the relative humidity and the percentage of injected CO_2. The temperature is controlled using a thermostatically controlled bath while relative humidity is achieved by means of a saline type $Ca(NO_3)_2.4H_2O$.

According to Thiery [16], accelerated carbonation tests show it is unrealistic to conduct trials with a low CO_2 content (less than 5%) because, at this level, the speed of carbonation is very sensitive to small changes in the CO_2 content: that's why he worked with 50% CO_2. Studies by Monkman and Shao [4] suggest the same amount of CO_2 in insisting on the fact that, in the air, the CO_2 concentration is between 0.03% and 0.05%. The second study suggests the use of an incubator where the relative humidity is about 60%, which is the most common.

Incubators available in the lab allowed to work with rate of 20% and commercial CO_2 [14]. The principle of the injection test device (Fig. 2) is as follows: the pressure vessel, with a volume of 0.04 m³ and the available pressure of 5 MPa, serves as a source of CO_2. The mixture of air with carbon dioxide is performed in another container for a volume of 0.3 m³ and a pressure up to 1 MPa. The gas mixture is transported by pipes through the ceiling of the incubator and the gas diffuses through holes in the ceiling and floor. The constant pressure in the range between 150 and 200 Pa is maintained in the sealed chamber by the automatic control equipment. The fans are placed inside of the tank and in the rooms, to ensure a constant concentration of carbon dioxide, which is heavier than air. The concentration of CO_2 is registered by detection tubes with a precision of 0.5% [17].

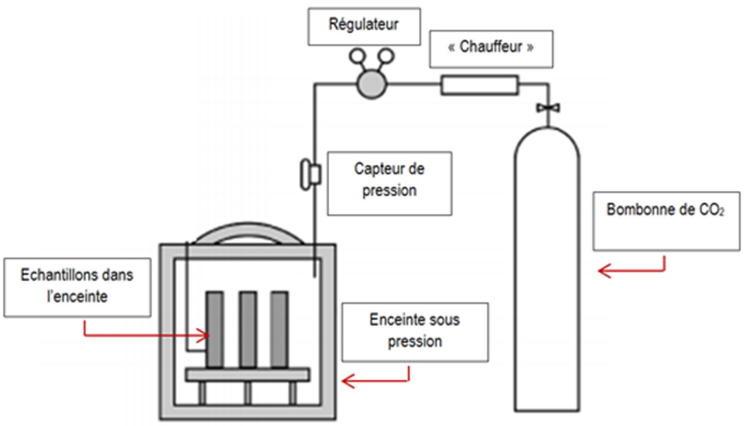

Figure 2: System for CO_2 incubation [18]

5. CO_2 ABSORPTION EVALUATION

It is possible to quantify CO_2 absorption by means of the calculation of the mass variation of the sample, according to Monkman's relationship [6]:

$$\text{Mass gain (\%)} = (\text{mass}_{final} + \text{mass}_{loss\ water} - \text{mass}_{initial})/\text{mass}_{dry\ binder} \qquad \text{(eq.1)}$$
$$= \Delta\ \text{mass}_{CO2}/\text{mass}_{dry\ binder}$$

The mass of water is taken into account because the test is performed in a closed system: a device is set up to capture water lost by concrete blocks. We assume that the aggregates are inert in relation to the capture of CO_2. The mass of the sample is measured after 1, 3 and 7 hours for the first tests in order to avoid too often opening the incubator. The measurement is made after 16, 24, 32 and 48 hours, respectively.

During the introduction of concrete blocks in the incubator, they will reject water; discharged water is measured using silica gel, whose main property is to capture the water in a wet environment. The silica gel will capture the concrete blocks water but also water from saline solution. This absorption is evaluated on the base of the change in mass of silica gel one day left in the incubator without concrete blocks in the curing conditions of accelerated carbonation (60% relative humidity and 20% CO_2 injected).

6. RESULTS AND DISCUSSIONS

6.1 Carbonation of miscanthus aggregates

After mineralization process which includes cement, silica fume, $CaCl_2$ and superplasticizer, miscanthus aggregates are stored into incubator (Fig. 2) for 7 hours and mass increase is registered for 1, 3 and 7 hours, respectively. Aggregates are disposed in such a way that CO_2 is able to diffuse from all the faces. Quantification of CO_2 gain mass (Table 3) is based on Monkman equation (Eq. 1).

Table 3 Quantification of CO_2 absorption by miscanthus aggregates

Variables	Sample 1	Sample 2	Sample 3	Total
Initial mass (g)	363.52	422.34	325.37	1111.23
Final mass (g)	363.20	421.95	325.06	1110.21
Water loss mass (g)	6.34	7.37	5.68	19.40
Dry binder mass (g)	118.80	138.02	106.33	363.15
Mass gain (%)	5.07	5.06	5.05	5.06

The initial and final masses are obtained by registering mass performed every x hours (Table 4). The loss of mass of water is obtained for all of the samples, by summing the increase of masses of silica gel and saline (both water absorber). Thus, we can get the mass of water lost in the samples as equivalent to that captured by the silica gel and saline simultaneously. The calculation is as follows (eq. 2):

$$\text{Mass}_{\text{water lost}} = \text{Final mass}_{\text{silica gel}} + \text{final mass}_{\text{saline solution}} - (\text{initial mass}_{\text{silica gel}} + \text{initial mass}_{\text{saline solution}}) \quad \text{(eq.2)}$$

Calculation of water lost for all the samples is: 208.2 + 2436.6 – (200 + 2425.4) = 19.4 gram. The assumption is made that the sample loses water in proportion to its mass. Indeed, there are 3 samples in the incubator, it does not seem correct to say that each sample loses one third of the total water. Indeed, since the sample 1 represents 32.71% mass of all samples in the incubator, we consider that the mass of water lost by the sample is 32.71% of the mass of water lost by all samples. Thus, the mass of water lost by the sample 1 is calculated as follows: (32.71/100)x19.4 = 6.34 gram.

As we exactly know the quantity of cement used for mineralization, it is possible to know the mass of dry binder (eq. 3):

$$\text{Mass}_{\text{dry binder}} = \text{percentage}_{\text{theory}} \times \text{mass}_{\text{initial}} \quad \text{(eq.3)}$$

For example, for sample 1, it gives: (32.68/100) x 363.52 = 118.80 gram

The mass gain calculated with eq. 3 is around 5%, with a good reproducibility. Another interesting item is to verify how fast and long is CO_2 diffusion with time (Table 4).

Table 4 CO_2 mass gain (%) vs time

Time	Mass gain (%)		
	Sample 1	Sample 2	Sample 3
1 hour	1.32	1.29	1.36
3 hours	2.92	2.86	2.91
7 hours	5.06	5.06	5.05

We note a good reproducibility of results and we find that the absorption of CO_2 is increasing with time (Fig. 3).

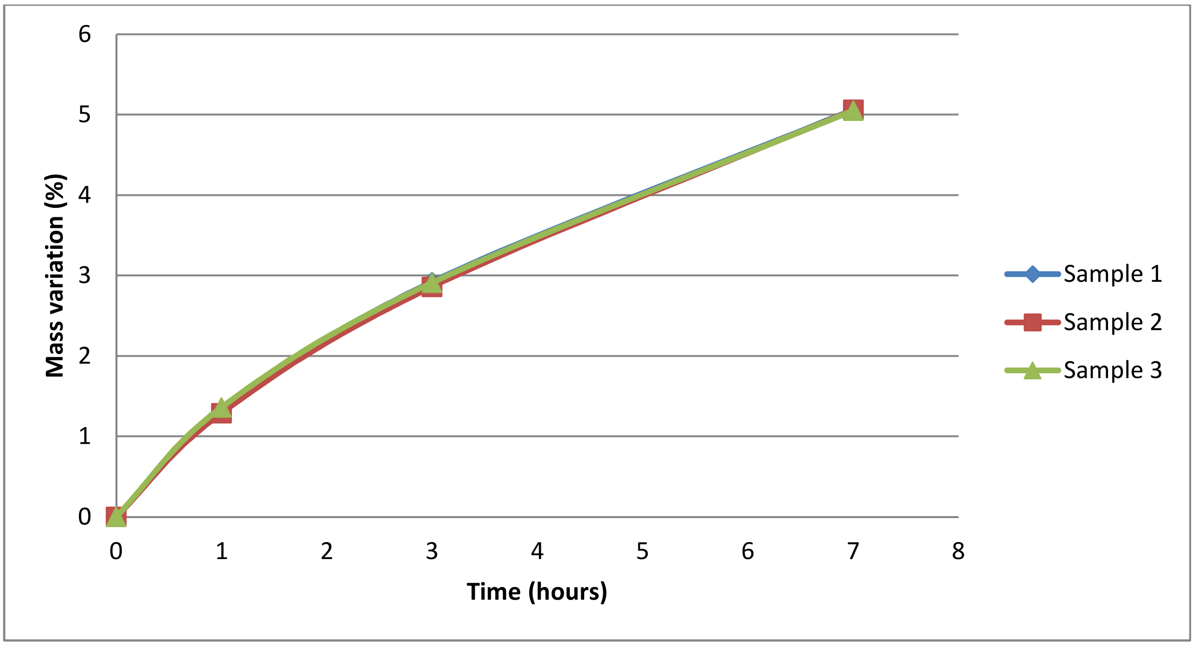

Figure 3: Evolution of CO_2 capture vs time

Moreover, we note that miscanthus carbonated aggregates are more resistant to wear than those who were not carbonated (Table 5). A Micro-Deval test was performed on the miscanthus chips. This test was adapted to vegetal fibers following the procedure adopted by Grimont to avoid the total destruction of the fibers [12]. 250 grams of miscanthus aggregates were introduced in the cylinder with 50 stainless steel balls. It was then rotated at 100 rpm for 10 minutes. Results showed that carbonated chips have a Micro-Deval coefficient of about 7.23, while those that were not carbonated get a coefficient approaching 12.69, which corresponds to a higher loss of mass during attrition process. We can say that the CO_2 capture on plant fibers miscanthus type is positive from mechanical point of view and should positively influence the compressive strength of blocks.

Table 5 Adapted Micro-Deval value for miscanthus

Material	Adapted Micro Deval coefficient			
	Sample 1	Sample 2	Sample 3	Average
Miscanthus aggregates	12.04	12.84	13.19	12.69
Carbonated miscanthus aggregates	7.98	6.70	7.01	7.23

6.2 Carbonation of concrete blocks

Concrete blocks were stored in two types of curing conditions during 7 hours:

- wet climatic room (100% R.H.),
- incubator with 20% CO_2.

Table 6 Compressive strength of concrete blocks

	Compressive strength (N/mm²)		**CO_2 mass gain (%)**
Test	Wet Curing	CO_2 Curing	
Miscanthus aggregates			
1	0.0091	0.0522	1.49
2	0.0091	0.0689	1.14
3	-	0.0546	1.36
Average	0.0091	0.0586	1.33
Carbonated miscanthus aggregates			
1	0.0275	0.202	1.43
2	0.0285	0.209	1.23
3	0.0314	0.205	1.37
Average	0.0290	0.205	1.34

Compressive strength of blocks (Table 6) is 5 times higher when stored in CO_2 incubator, even if it is quite low. But the objective is to obtain insulation materials and not structural elements. The average compressive strength of the blocks with carbonated miscanthus aggregates is almost 7 times as large as the blocks stored in a humid chamber. It is also four times greater than that of concrete blocks made from non-carbonated mineralized miscanthus.

7. CONCLUSIONS

On the basis of the experimental results, the following conclusions can be drawn:

- use of bio sourced materials like miscanthus requires a mineralization process in order to guarantee a minimum of rigidity and to reduce water absorption capacity;
- mineralization induces a better resistance to abrasion, which is profitable during mixing operations ;
- carbonation of bio sourced aggregates before concrete blocks production can increase concrete blocks performances;
- the compressive strength of concrete blocks is increased by using CO_2 injection, with regard to classic humid curing;

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